SILICON CARBIDE SUBLIMATION SYSTEMS AND ASSOCIATED METHODS

FIELD OF THE INVENTION

The present invention relates to the growth of crystals and, more particularly, to the growth of silicon carbide crystals.

BACKGROUND OF THE INVENTION

Over the last decade, the use of silicon carbide as a semiconductor material has grown dramatically. Silicon carbide semiconductors have certain properties, including a wide bandgap, high thermal coefficient and capacity to operate at far higher temperatures than certain common semiconductor materials, such as silicon, which are desirable in various semiconductor applications.

In many applications, it is desirable to use an underlying semiconductor material that is substantially of a single polytype (silicon carbide can, at least theoretically, form at least 150 different types of crystal lattices or "polytypes"). Additionally, it is typically preferable that the semiconductor material have low levels of defects in the crystal lattice and/or low levels of unwanted impurities. In fact, even in a pure material, a defective lattice structure can prevent the material from being useful for electrical devices, and the impurities in any such crystal are preferably controlled to give certain desired electrical characteristics (such as an n or p character). As such, the availability of appropriate silicon carbide crystals is generally desired for the successful manufacture of electrical devices from silicon carbide. Additionally, because of cost considerations, it is desirable to grow relatively large silicon carbide crystals, from which a large number of "wafers" may be produced. Cost and device specific considerations also make it desirable that these wafers have a relatively large surface area.

Traditionally, two broad categories of techniques have been used for forming crystalline silicon carbide for semiconductor applications. The first of these techniques is known as chemical vapor deposition ("CVD") in which reactant gases are introduced into a system to form silicon carbide crystals upon an appropriate substrate. The second main technique is generally referred to as sublimation. In this technique, some type of solid silicon carbide material is generally used as a starting material. This starting material may be of one or more

different polytypes, and may or may not include particles of the same polytype as the polytype which is desired for the single crystal semiconductor material. The solid silicon carbide starting material is heated in a crucible until it sublimes, and the vaporized material is encouraged to condense, with the condensation intended to produce the desired crystal. Typically, this is accomplished by introducing a monocrystalline silicon carbide seed into the crucible and heating it to a temperature less than the temperature at which silicon carbide sublimes. A pioneering patent that describes methods for forming crystalline silicon carbide for semiconductor applications using such sublimation techniques is U.S. Patent No. 4,866,005 to Davis *et al.*, issued September 12, 1989, which was reissued as U.S. Patent No. Re. 34,861, issued February 14, 1995, which patents are incorporated herein by reference as if set forth in their entirety.

SUMMARY OF THE INVENTION

According to embodiments of the present invention, methods of growing silicon carbide are provided. Pursuant to embodiments of the present invention, these methods use an electric arc to sublime a silicon carbide source material. In these embodiments, a silicon carbide seed crystal is introduced into a sublimation system, along with first and second electrodes that are separated by a gap. A power supply is coupled to at least one of the electrodes and used to create an electric arc across the gap between the two electrodes. This electric arc is used to sublime at least a portion of a silicon carbide source material. The vaporized silicon carbide material may then be encouraged to condense onto a seed material to produce silicon carbide. In embodiments of the present invention, at least one of the electrodes is comprised of silicon carbide and serves as the silicon carbide source material.

In specific embodiments of the present invention, methods of growing silicon carbide are provided in which a silicon carbide source is electrically arced to sublime silicon and carbon containing material from the silicon carbide source and cause at least some of the silicon and carbon containing material to form silicon carbide on a silicon carbide seed. In certain of these embodiments, the electrical arc may be established between a pair of spaced apart silicon carbide electrodes. In forming silicon carbide pursuant to these methods, the power dissipated across a gap between the pair of spaced apart silicon carbide electrodes

may be controlled to control the flow of vaporized Si, Si_2C and SiC_2 from the pair of silicon carbide electrodes to the silicon carbide seed. In certain embodiments, this flow of vaporized Si, Si_2C and SiC_2 per unit area per unit time from the pair of silicon carbide electrodes to the silicon carbide seed is controlled to be substantially constant.

In other embodiments of the present invention, the power dissipated across the gap is controlled by moving at least one of the pair of silicon carbide electrodes as they vaporize during the sublimation process to maintain a constant gap between the pair of silicon carbide electrodes. In specific embodiments, this control of the power dissipated across the gap may be accomplished by sensing the voltage drop across and/or the current through the gap and adjusting the relative location of the silicon carbide electrodes so as to maintain the voltage drop at a constant level. In yet other embodiments, the pressure within the sublimation system may be maintained at a substantially constant level during the sublimation process. These sublimation processes may occur within a heated furnace, and the internal temperature of the furnace, the position of the pair of silicon carbide electrodes, the voltage drop across the spacing between the pair of silicon carbide electrodes and the arc current may be configured so as to maintain the ends of the pair of silicon carbide electrodes adjacent the arc at a substantially constant temperature during the sublimation process.

In still further embodiments of the present invention, methods of growing silicon carbide are provided in which a furnace is heated to a temperature below the temperature at which silicon carbide sublimes, and a local high temperature zone is created within the furnace that is above the temperature at which silicon carbide sublimes. In these embodiments, a silicon carbide source material may be introduced into the high temperature zone to sublime silicon and carbon containing material from the silicon carbide source and cause at least some of the silicon and carbon containing material to form silicon carbide on a silicon carbide seed.

In other embodiments of the present invention, methods of growing silicon carbide are provided in which a seed of silicon carbide, a silicon carbide electrode and a second electrode are introduced into a sublimation system. The electrodes are positioned such that they are separated by a gap. In these embodiments, an electric arc may be established across the gap between the silicon carbide electrode and the second electrode to vaporize at least part of the silicon carbide electrode

and cause at least some of the vaporized silicon carbide materials to form silicon carbide on the silicon carbide seed.

Sublimation systems which may be used in performing these methods are also disclosed herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of an electric arc silicon carbide sublimation system according to embodiments of the present invention.

Figure 2 is a flow chart depicting methods of growing crystals of a single polytype of silicon carbide according to embodiments of the present invention.

Figure 3 is a flow chart depicting methods of growing crystals of a single polytype of silicon carbide according to additional embodiments of the present invention.

Figure 4 is a schematic diagram of an electric arc silicon carbide sublimation system according to alternative embodiments of the present invention.

Figure 5 is a schematic diagram of an electric arc silicon carbide sublimation system according to alternative embodiments of the present invention.

Figure 6 is a schematic diagram of a silicon carbide sublimation system according to alternative embodiments of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like numbers refer to like elements throughout.

In the present disclosure, a first element or component is sometimes referred to as being located or positioned "on" a second element or component. It will be appreciated that such references are intended to encompass both situations where the first element or component is located directly on the second element or component and where the first element or component is located on the second element or component through intervening structure(s).

Systems and methods according to embodiments of the present invention grow silicon carbide crystals using electric arc sublimation. Pursuant to embodiments of the systems and methods disclosed herein, the silicon carbide source material used in the sublimation process comprises at least one silicon carbide electrode, and this source material is sublimed by creating an electric arc between the silicon carbide electrode and a second electrode that raises the temperature of the silicon carbide electrode adjacent the arc to a temperature sufficient to sublime the silicon carbide. In other embodiments, a localized heat source is used instead of an electric arc to raise a portion of a silicon carbide source material to a temperature at which it sublimes.

In the electric arc embodiments of the present invention, by controlling the power dissipation across the electric arc, it may be possible to control the flow of vaporized Si, Si_2C and/or SiC_2 from the silicon carbide source to a seed independent of both the internal temperature and/or pressure of the sublimation system. As a result, the temperature and pressure of the sublimation system may be set to grow a desired polytype of silicon carbide, as opposed to conventional silicon carbide sublimation techniques where the pressure and/or temperature may need to be adjusted throughout the process in an effort to maintain a relatively constant source-to-seed flux of the vaporized silicon carbide.

As will be appreciated by those of skill in the art, silicon carbide may be monocrystalline (*i.e.,* silicon carbide that is substantially of a single polytype, although it may include defects in the crystal lattice, impurities, and small areas of other polytypes) or polycrystalline. The methods and systems of the present invention may be used grow both monocrystalline and polycrystalline silicon carbide. It will further be appreciated that monocrystalline silicon carbide is typically preferred in applications where the silicon carbide is used to form semiconductor devices. In such applications, monocrystalline silicon carbide is typically grown on a monocrystalline silicon carbide seed crystal.

Figure 1 depicts a sublimation system **100** according to embodiments of the present invention. As shown in **Figure 1**, the sublimation system **100** includes a high temperature furnace **102**. Furnace **102** comprises side insulating walls **104,** a bottom insulating wall **106**, and a top insulating wall **108**. The furnace **102** further includes a plurality of heating elements **112**, **112'** and a seed holder **114**. The seed holder **114** may have in and out coolant feeds **113** which may be used to

control the seed gradient and the growth rate of the silicon carbide. As indicated in **Figure 1**, the heating elements **112, 112'** may comprise resistive heating elements disposed along the side insulating walls **104** of the furnace **102**. However, other heating such as radiant heating may be used. The furnace **102** may also include two recesses **122, 124** in the side insulating walls **104**. A gas feed **160** in conjunction with a pressure control mechanism (reference numerals **162, 163, 164, 166, 168** in the embodiment of **Figure 1**) may also be provided to facilitate establishing the pressure within the furnace at a desired level or levels. A pyrometer **199** may be used to measure the temperature at the seed **140** and/or at the seed holder **114**. Other methods of measuring this temperature may also be used (e.g., thermocouples).

The sublimation system **100** further includes a pair of silicon carbide electrodes **130, 132**. As shown in **Figure 1**, the electrodes **130, 132** may be positioned in the respective recesses **122, 124**. The electrodes **130, 132** are positioned such that they are separated by a gap **134**. Silicon carbide electrode **132** is coupled to a grounded power supply **136**, and silicon carbide electrode **130** is coupled to ground. However, it will be understood that other power supply arrangements could be provided, including providing multiple alternating current and/or direct current power supplies, or a combination thereof, that are attached to one or both electrodes **130, 132**.

The silicon carbide electrodes **130, 132** may be configured in a variety of different shapes and sizes. By way of example, the electrodes may be rods having circular, square, rectangular or other cross-section, and the length of the electrodes **130, 132** may be established based on the amount of source material required. Alternatively, a rotating disk of silicon carbide might be used, which might facilitate providing a larger charge of silicon carbide source material in a furnace **102** of a given size, and may provide for finer control of the incremental movement of the electrodes discussed herein.

Sublimation system **100** may be operated as follows. The sublimation system **100** is evacuated of gases, and an inert gas such as argon, helium, xenon or the like may be input into the chamber. Those of skill in the art will appreciate that the sublimation system **100** may be operated with other gases or combinations of gases (e.g., adding a little hydrogen with an inert gas) in the chamber, or under vacuum conditions as well. The resistive heating elements **112, 112'** are turned on

to raise the inside temperature of furnace **102** to a temperature somewhat less than the temperature at which silicon carbide sublimes. As will be understood by those of skill in the art, the temperature at which sublimation occurs may depend on a variety of factors, including the pressure inside the furnace **102**, and the polytype composition of the silicon carbide source material. Typically, the resistive heating elements **112'** adjacent the seed holder **114** are set at a lower temperature (*e.g.*, 20 °C lower) than the temperature of the remaining heating elements **112**. Such a temperature differential may facilitate maintaining the furnace temperature adjacent the seed holder **114** at a temperature lower than the temperature of other locations within the furnace **102**. This may help ensure that the silicon carbide vaporized during the sublimation process tends to condense on the seed **140** placed on seed holder **114**. Typically, the heating elements 112, 112' are operated at a temperature higher that the temperature at which silicon carbide will sublime to a solid form. In this manner, the tendency for the silicon carbide vapor to condense in areas within the chamber other than the seed holder can be minimized or prevented.

It will also be appreciated that the sublimation pressure may be operated under constant or variable pressure conditions. Changes in pressure may be implemented by changing the flow rate at which gases are introduced into the chamber or by changing the rate at which gases are evacuated from the chamber. As will be appreciated by those of skill in the art, it may be advantageous to decrease the pressure during growth in order to attempt to maintain a constant flux between the source silicon carbide material and the seed **140** as the source material is slowly being depleted.

Prior to activating resistive heating elements **112, 112'**, a silicon carbide seed crystal **140** is placed on the seed holder **114**. The furnace **102** may also be pressurized to a pre-selected pressure. The furnace **102** is heated to an appropriate temperature and power supply **136** may be activated, causing a current to flow through silicon carbide electrode **132**. The gap **134** between the electrodes **130, 132** and the setting on the power supply **136** are configured so that the current flowing through electrode **132** creates, and flows across, an electric arc **142** between silicon carbide electrode **132** and silicon carbide electrode **130**, and then flows through silicon carbide electrode **130** to electrical ground (in the exemplary embodiment of **Figure 1**).

The electric arc **142** acts to increase the temperature of the ends **130'**, **132'** of the electrodes **130, 132**. This increase in temperature may be sufficient to raise the ends **130', 132'** of electrodes **130, 132** to a temperature above the temperature at which silicon carbide sublimes (given the pressure level within the furnace **102**). As indicated by the upwardly pointing arrows in **Figure 1**, as the silicon carbide electrodes sublimes, it can form up to three or more basic vaporized materials: Si, Si_2C and SiC_2. Depending upon the polytype of the source powder used to form the silicon carbide electrodes **130, 132** (see discussion herein), the amount or "flux" of each of the species that is generated may differ. As used herein, the term "flux" refers to the amount of matter or energy passing through a designated plane of a given area during a given period of time. Accordingly, when used to describe the flow of vaporized species, flux can be measured and designated in units of matter, area and time such as grams per square centimeter per second ($g/cm^2/sec$).

As shown in **Figure 1**, the vaporized Si, Si_2C and/or SiC_2 flow from the electrodes **130, 132** toward the seed **140**. As the seed **140** is maintained at a temperature below which silicon carbide sublimes, the vaporized Si, Si_2C and/or SiC_2 tend to condense onto the seed, resulting in macroscopic growth of silicon carbide that may be substantially of a desired polytype. Typically, the seed holder **114** will rotate the seed **140** during the sublimation process to encourage uniform growth across the surface area of the seed **140**.

As is also shown in **Figure 1**, the sublimation system **100** may further include a flux control system, which in the embodiment of **Figure 1** comprises the items labeled **152, 154, 156**. This flux control system **152, 154, 156** may be provided to facilitate maintaining a substantially uniform flow of Si, Si_2C and/or SiC_2 of consistent composition from the silicon carbide electrodes **130, 132** to the seed **140**, and will be described in detail below. As will be understood by those of skill in the art, such a uniform, consistent composition, flow of the vaporized species of silicon carbide can facilitate the growth of monocrystalline silicon carbide on the seed **140**. Such monocrystalline structures are generally preferred for semiconductor applications.

As the ends **130', 132'** of silicon carbide electrodes **130, 132** sublime, the gap **134** between the two electrodes **130, 132** increases. This increase in the size of the gap **134** may result in a decrease in the current flowing across the gap from electrode **132** to electrode **130**, as the voltage required to maintain a specific

current level may increase with the size of the gap **134**. As the current flow across the gap **134** decreases, the temperature of the ends **130'**, **132'** of electrodes **130, 132** likewise may decrease, which may result in a reduction of the flow of Si, Si_2C and/or SiC_2 from the silicon carbide electrodes **130, 132** to the seed **140**. Flux control system **152, 154, 156** may operate to reduce and preferably prevent such a reduction in flow of Si, Si_2C and/or SiC_2 from occurring.

In the embodiment of sublimation system **100** depicted in **Figure 1**, the flux control system comprises a voltage detector **152**, a pair of motorized electrode positioners **154** and a processor **156**. Voltage detector **152** measures the voltage across the gap **134**. Voltage detector **152** could be implemented as an integral part of the power supply for the electrodes or as an independent unit used to control the output voltage of the power supply. The output of voltage detector **152** is fed to processor **156**, which determines the incremental change in the position of one or both of the electrodes **130, 132** which is required to maintain the voltage across the gap **134** at its original level. Processor **156** may determine this incremental change value in a variety of ways, including, for example, by use of a look up table or by positive feedback from the voltage detector **152** in response to small changes in the position of the electrodes **130, 132**. The motorized electrode positioners **154** are responsive to the processor **156** and implement the actual change in the relative positions of the electrodes **130, 132**. Typically an electrode positioner **154** will be associated with each electrode **130, 132** so that the gap **134** may be maintained directly below the seed **140** throughout the sublimation process. The flux control system **152, 154, 156** in the embodiment of **Figure 1** thus may be used to maintain a substantially constant flow of Si, Si_2C and/or SiC_2 by maintaining the length of gap **134** at a constant value so that constant power dissipation occurs across the gap **134**.

Electronic monitoring and control systems comprising a voltage detector, motorized positioners and a processor are commercially available, such as, for example, the units which are used to create intense light sources for developing offset printing negatives in the lithography industry. It will also be appreciated that a current meter that detects the current across the arc **142** and/or a thermometer that measures the temperature at or directly adjacent to the ends of the silicon carbide electrodes **130, 132** as they are positioned at the beginning of the sublimation process could be used instead of, or in addition to, the voltage detector

152, as could a variety of other detection devices. Likewise, a mechanical, optical or other type of measuring system could be used to measure or estimate the length of gap **142**.

In an alternative embodiment of the present invention, the flux control system may not include the voltage detector **152** or the processor **156**. In this embodiment, the rate of erosion of the silicon carbide electrodes **130, 132** during sublimation is determined in advance, and the motorized electrode positioners **154** are set to incrementally move the electrodes **130, 132** at a rate that compensates for the erosion. In this embodiment of the invention, it may be desirable, in some instances, to carefully select electrodes **130, 132** based on density, source polytype and/or any other parameter that may effect the rate of erosion under given furnace temperature and pressure and arc voltage and current conditions.

In yet another embodiment of the present invention, the current across the gap **134** may be maintained during the sublimation process by increasing the setting on the power supply **136** as opposed to by moving the electrodes **130, 132** to maintain a constant gap size as the ends **130', 132'** of the electrodes **130, 132** sublime. In this embodiment, the actual size of the gap **134** would increase throughout the sublimation process, but the current would be maintained by sensing the voltage and/or current drop that starts to occur as the ends **130', 132'** of the electrodes **130, 132** sublime, and increasing the power supplied to electrode **132** to compensate for such decreases. However, it may be preferable to maintain the constant current across the gap **142** by physically moving the electrodes **130, 132** as is done in the embodiment of **Figure 1** as opposed to by increasing the setting on power supply **136**, as the increase in gap size may change the flow patterns of the vaporized Si, Si_2C and/or SiC_2 and/or the surface area of the electrodes **130, 132** which reach sublimation temperatures, both of which may result in non-uniform flow of Si, Si_2C and/or SiC_2 or flow with inconsistent composition from the electrodes **130, 132** to the seed **140** during the sublimation process.

It will also be appreciated that various combinations of the above-described embodiments of the present invention may be employed, or that multiple of the measurement/detection techniques and/or mechanisms for keeping a substantially constant current flow across the gap **142** may be employed in a single system. Those of skill in the art will also appreciate in light of the present disclosure that

additional measurement/detection techniques and/or mechanisms for keeping a substantially constant current flow across the gap **142** other than the exemplary embodiments disclosed herein may be employed that will still provide the benefits of the present invention.

In embodiments of the present invention, the gap **134** between the first and second electrodes **130**, **132** is between 0.2 mm and 5.0 mm. However, it will be appreciated that gaps of other dimensions may be provided as the gap size selected depends, among other things, on the electrode voltage and system pressure. Gaps larger than 5.0 mm may be used, but larger gaps may require higher voltage settings on the power supply to maintain the desired current flow across the gap. Additionally, as the gap increases beyond a certain range, it may be difficult to maintain the current flow at a constant level due to the limits of the output potential of the power supply.

Likewise, a wide range of different arc current levels may work well in the sublimation systems of the present invention. The current level used may depend on a variety of factors, including, for example, the internal temperature and pressure of the furnace **102**, the desired rate of vaporization, and the composition of the electrodes **130**, **132**.

As will be appreciated by those of skill in the art in light of the present disclosure, the sublimation systems and methods of the present invention can provide a way to control the flow of Si, Si_2C and/or SiC_2 from the electrodes **130, 132** to the seed **140** that can be independent of the pressure within the furnace **102**, and which can be at least partly independent of the temperature settings within the furnace **102**. As such, the pressure during sublimation and, to some extent, the temperature, may be set to select a desired polytype of silicon carbide that is to be grown and/or to reduce the number of defects in the grown crystal. In contrast, current silicon carbide sublimation systems may reduce the pressure within the crucible throughout the sublimation process in an effort to maintain the source-to-seed flow of Si, Si_2C and/or SiC_2 at a relatively constant level. Such a reduction in pressure may be used because as the source silicon carbide powder charge depletes, the volume/surface area which is subliming at any given point also typically decreases. Consequently, to maintain substantially constant flux for extended periods of time it may be desired to increase the temperature within the sublimation system and/or decrease the pressure. Such modifications to the

temperature or pressure within the sublimation system, however, can adversely effect the monocrystalline nature of the silicon carbide grown on the seed **140** in applications where it is desired to grow monocrystalline silicon carbide.

Additionally, under certain temperature/pressure conditions, it is known that certain types of defects tend to grow in various polytypes of silicon carbide. Accordingly, if the temperature and/or pressure are adjusted during sublimation using conventional sublimation techniques in an effort to maintain a constant flow of Si, Si_2C and/or SiC_2 during the sublimation process, temperature and/or pressure conditions may be in place for portions of the process that tend to encourage the growth of defects. Furthermore, when conventional sublimation techniques are used, the composition of the flux tends to change over time (*i.e.*, it does not have a consistent composition) as certain elements or compounds are depleted from the charge in the crucible. Such inconsistencies in the composition of the flux may also adversely effect the quality of the crystal grown. However, pursuant to the teachings of the present invention the degree of such inconsistencies can be reduced, as the limited amount of source material that is raised to a sublimation temperature at any given time may provide for consistent depletion of specific elements/compounds in the source material.

In this regard, the volume and surface area of the silicon carbide electrodes which sublime at any given time during the sublimation process may be controlled by providing electrodes **130**, **132** which are substantially the same shape, composition and density throughout their length. By using such electrodes **130**, **132**, and by maintaining the furnace **102** temperature and pressure constant, as well as the current transferred across the arc **142**, generally the same volume and surface area of electrodes **130**, **132** will be raised to a sublimation temperature at any given time during the sublimation process. However, it will be understood that in the shape, composition and/or density of the silicon carbide electrodes **130, 132** could be variable as well, and in certain applications it may even be advantageous to provide such variability to offset other effects during the sublimation process.

A preferred or optimum pressure level for the sublimation process may depend on a number of factors, including, for example, the polytype of silicon carbide that is to be grown, the characteristics of the seed **140** used, the internal temperature of the furnace **102**, and the power dissipated across the gap **134**. Depending upon these factors, pressures from just a fraction of atmospheric

pressure to five, ten or even more times higher than atmospheric pressure may be preferred.

As noted above, the flow of Si, Si_2C and/or SiC_2 from the electrodes **130**, **132** to the seed **140** may only be partly independent of the temperature within the furnace **102**. The flow control may not be completely independent of the temperature inside the furnace **102** because the temperature caused by the current flow through the arc **142** can raise the temperature of the respective ends **130'**, **132'**of silicon carbide electrodes **130**, **132** to a temperature at which they start to sublime. Additionally, the temperature of the furnace walls **104**, **106**, **108** should also be sufficiently high such that the vaporized Si, Si_2C and/or SiC_2 tends to condense of the seed **140** instead of on the walls **104**, **106**, **108**.

It will be appreciated that a wide variety of furnaces may be employed in the sublimation systems of the present invention. Typically, the furnace should be capable of heating to temperatures in excess of 2000 °C and, more preferably, to at least 2500 °C, to allow for silicon carbide sublimation at a wide variety of pressure levels. In an exemplary situation, the interior of the furnace might be heated to a temperature on the order of 2300 °C, while the seed crystal **140** might be heated to a temperature on the order of 2280 °C. However, it will be understood that sublimation and condensation are equilibrium processes that may be affected by the vapor pressure of the system as well as the absolute and relative temperatures. Accordingly, it will be understood that in the processes and systems described herein, the appropriate temperatures generally will be a function of the selected vapor pressure level (and vice versa).

Furnaces suitable for use in the sublimation systems of the present invention are commercially available, such as the Crystal furnace, manufactured by Centorr/Vacuum Industries. Such furnaces may be modified to facilitate mounting the silicon carbide electrodes **130**, **132** and to provide for mounting of the flux control system components within and/or outside the furnace **102**.

Moreover, the furnace **102** may use heating techniques other than resistive heating, such as induction heating. Likewise, a variety of configurations may be employed for locating the silicon carbide electrodes **130, 132** with respect to the seed **140**, and for locating the various heating elements **112, 112'** used. Additionally, channeling walls **120**, or some other means for channeling the flow

of vaporized Si, Si_2C and/or SiC_2 in a preferred direction may be provided. Typically, the walls **104**, **106**, **108** of the furnace **102** are formed of insulating material such as, for example, graphite.

The furnace **102** may include recesses such as recesses **122, 124** in **Figure 1** into which the silicon carbide electrodes **130, 132** may be inserted. Such recesses may allow for the use of large electrodes (*e.g.,* 4 feet in length) which may extend outside the main chamber of the furnace **102**. In this manner, significantly larger amounts of silicon carbide source material may be provided for the sublimation process, as the charge holder in conventional sublimation crucibles is typically limited in volume. Accordingly, it will be appreciated that the methods and systems of the present invention can facilitate growing larger diameter crystals and larger boules.

Additionally, as noted above, it will also be appreciated that in conventional silicon carbide sublimation systems, the location of the source material within the crucible may impact the uniformity and/or the consistency of the flow of Si, Si_2C and/or SiC_2 from the source to the seed, as temperature variations may exist adjacent different portions of the charge which, as the charge is depleted, may cause variation in the flux. Such variations may be compounded as larger crucible designs (having increased charge capacity) are employed, particularly to the extent a thermal gradient exists between the source material and the interior of the furnace **102** just above the seed **140**. In contrast, pursuant to embodiments of the methods and systems of the present invention, only the area adjacent the gap **134** may need to be raised to a temperature at which silicon carbide sublimes. Consequently, it is possible to maintain a relatively constant volume/surface area of silicon carbide that is raised to a sublimation temperature throughout the entirety of the sublimation process by maintaining the ends **130'**, **132'** of the silicon carbide electrodes **130, 132** in the same position throughout the sublimation process via incremental movement. It will be understood, however, that other locations in the furnace may be raised in temperature as well. Additionally, a crucible need not be used as the sublimation process may instead take place directly within the confines of the furnace **102**.

As noted above, the pressure and temperature within the furnace **102** may be pre-selected to encourage the growth of a specific polytype of silicon carbide and/or to otherwise optimize growth conditions. In the embodiment of **Figure 1**, a

gas feed **160** is used to establish the pressure within the furnace **102**, along with vacuum pump **162**, valve **164**, pressure transducer **166** and controller **168**. Specifically, gas feed **160** is used to feed a pressurized gas such as argon into the interior of furnace **102**. Various other gases (which need not be inert) may also be used. Pressure transducer **166** senses the pressure within the furnace **102** and relays this information to the controller **168**. The controller **168** controls valve **164** which is placed across an outlet **163** provided in the top of the furnace **102**. Once the desired pressure has been reached inside the furnace **102**, controller **168** incrementally opens valve **164**. The vacuum pump **162** is situated on the opposite side of the valve **164**, and is configured to draw gas out of the interior of furnace **102**. Via feedback provided by pressure transducer **166**, controller **168** opens the valve **164** a sufficient amount to equalize the pressure within furnace **102** given a constant feed of gas into the furnace via gas feed **160**. However, other pressurization systems and/or gases (or a vacuum) may be used.

As noted above, power supply **136** may be either a direct current ("DC") or alternating current ("AC") power supply. Pursuant to the teachings of the present invention, it will be understood that forming the arc **142** using a DC power supply may be desirable in certain embodiments, such as ones in which dissimilar electrode materials (*e.g.,* silicon carbide and tungsten, graphite or molybdenum) are used. However, under certain circumstances (*e.g.,* pressure and temperature conditions, electrode composition, current values, etc.), during the sublimation process the use of a DC power supply may encourage the electrodes **130, 132** to vaporize unevenly. Thus, in certain situations, use of an AC power supply may be preferred as the alternating nature of the power supplied serves to balance out any imbalance in the erosion characteristics of the electrodes **130, 132**. However, when an AC power supply is operated at certain frequencies, it may result in the silicon carbide source material vaporizing off of one electrode and then condensing on to the other electrode. Consequently, the frequency setting on the power supply will typically be set to a frequency that helps provide for balanced erosion, and that avoids transfer of silicon carbide from one electrode to the other. It will also be understood that a combination of AC and DC power supplies may be used (*e.g.,* connecting one electrode to an AC power supply and the other electrode to a DC power supply), and that the electrodes **130, 132** need not be grounded.

In sublimation systems in which a DC power supply is used, it may be advantageous to provide a second DC power source that is coupled to electrode **130** and set to an equal but opposite setting of the power supply **136**. This may help to reduce unequal erosion of the electrodes. Additionally, in situations where the silicon carbide electrodes **130, 132** are very pure (and hence have relatively poor intrinsic conductivity), it may be advantageous to use an AC power supply set at a high frequency as the high frequency, enhances the conductivity of the electrodes.

As noted above, in alternative embodiments of the present invention, the electric arc may be established between a silicon carbide electrode and another electrode that is not formed of silicon carbide. In these embodiments, the non-silicon carbide electrode could be formed of a variety of materials, including, for example, graphite, tungsten, molybdenum or tantalum carbide. Preferably, the non-silicon carbide conductor is formed of a material or materials that vaporize at higher temperatures than silicon carbide. **Figure 4** illustrates an exemplary embodiment of a sublimation system **400** according to the present invention in which an electric arc is established between a silicon carbide electrode **132** and a non-silicon carbide electrode **170**. In the particular embodiment of the invention depicted in **Figure 4** many of the components are identical to the corresponding components depicted in **Figure 1** (*i.e.,* the components having like numbers in **Figure 1** and **Figure 4**), and hence these like components will not be re-described here.

In the particular embodiment of **Figure 4**, the flux control system **152, 154, 156** is only configured to move one of the electrodes, namely silicon carbide electrode **132**. Such an arrangement may be preferred in embodiments in which non-silicon carbide electrode **170** does not vaporize during the sublimation process. However, it will be appreciated that the system can be configured such that both electrodes **132, 170** are repositioned during the sublimation process, or so that both electrodes remain stationary (as the flux may be controlled by means other than movement of the electrodes as discussed above with respect to the embodiment of **Figure 1**). As illustrated in **Figure 4**, the distal end **132'** of silicon carbide electrode **132** may be positioned so that it is directly below the silicon carbide seed **140**. However, it will also be appreciated that different positionings of the electrodes **132, 170** are also possible.

As is also discussed above, in still other embodiments of the present invention the electric arc may be established between two or more non-silicon carbide electrodes and a silicon carbide source material may be positioned adjacent the electric arc. In these embodiments, the non-silicon carbide electrode could be formed, for example, out of any of the materials listed above with respect to the embodiments of the present invention which incorporate a single silicon carbide electrode. **Figure 5** illustrates an exemplary embodiment of a sublimation system **500** according to the present invention in which an electric arc **142** is established between a pair of non-silicon carbide electrodes **180, 182** and a silicon carbide source material **184** is located adjacent the arc **142** formed between electrodes **180, 182**. It may be more difficult in such an embodiment to generate sufficient energy adjacent the arc **142** to cause the silicon carbide source material **184** to sublime. In the particular embodiment of the invention depicted in **Figure 5** many of the components are identical to the corresponding components depicted in **Figure 1** (*i.e.,* the components having like numbers in **Figure 1** and **Figure 5**), and hence these like components are not re-described here.

In the particular embodiment of **Figure 5**, the flux control system comprises a sensor **186**, a silicon carbide source material positioner **188** and a processor **189**. The sensor **186** may be used to measure a variety of parameters that are indicative as to the rate at which the silicon carbide source material **184** is subliming including, for example, the voltage across the arc **142**, the current through the arc **142**, the temperature adjacent the arc **142**, etc. This information is fed to a processor **189** which controls a material positioner **188** that moves the silicon carbide source material **184** closer to the arc **142** as the silicon carbide source material **184** sublimes. It will be appreciated that in a manner similar to the embodiment of **Figure 1**, either the position of the arc **142** or the position of the silicon carbide source material **184** may be varied as the silicon carbide source material **184** sublimes. Likewise, both the silicon carbide source material **184** and the arc **142** may remain stationary and the current through the arc **142** may instead be varied (see above discussion with respect to the embodiment of **Figure 1**).

In the embodiment of **Figure 5**, the furnace **102** may be heated to a temperature below the temperature at which silicon carbide sublimes. An electric arc **142** may be established between the electrodes **180, 182**, which may have the effect of increasing the temperature in a localized area adjacent the arc **142** within

the furnace **102**. The silicon carbide source material **184** may be positioned adjacent the arc **142**, so that a portion of the silicon carbide source material is within the localized area of increased temperature and is raised to a temperature at which silicon carbide sublimes. As this portion of the silicon carbide source material **184** sublimes, the sensor **186** senses the rate of sublimation and via processor **189** and positioner **188** acts to move either the silicon carbide source material **184** or the arc **142** (*e.g.*, by moving conductors **180, 182**) to maintain a relatively constant rate of vaporization of the silicon carbide source material. As with the embodiment of **Figure 1**, such a flux control system may also be omitted, by, for example pre-programming the silicon carbide source material **184** and/or the electrodes **180, 182** to move relative to each other such that the distance between the silicon carbide source material **184** and the arc **142** is maintained at a desired distance throughout the sublimation process.

In yet other embodiments of the present invention, a localized region within a furnace **102** may be raised to a temperature above the temperature at which silicon carbide sublimes by providing a localized heat source **190** within the furnace **102**. Such a localized heat source **190** could be implemented using, for example, an induction heating configuration localized to the end of the electrodes. **Figure 6** depicts an exemplary silicon carbide sublimation system **600** according to these embodiments of the present invention.

As illustrated in **Figure 6**, one end or region of a silicon carbide source material **192** is placed adjacent a localized heat source **190**. During the sublimation process, the localized heat source **190** may be used to raise this end or region of silicon carbide source material **192** to a temperature at which it sublimes. A flux control system (not pictured in **Figure 6**) may be used to control the temperature in the furnace adjacent the end of silicon carbide source material **192** to control the rate at which it sublimes. Such a flux control system may comprise, for example, positioning mechanisms that maintain the end of silicon carbide source material **192** at a constant distance from localized heat source **190** and/or a feedback mechanism that is used to increase the output temperature of localized heat source **190** as the distance between the localized heat source **190** and the silicon carbide source material **192** increases. As with the embodiments of the present invention depicted in **Figure 4** and **Figure 5**, the particular embodiment of **Figure 6** includes many components that are identical to the corresponding

components depicted in **Figure 1** (*i.e.*, the components having like numbers) and hence these like components will not be re-described here.

It will be appreciated to those of skill in the art in light of the present disclosure that various combinations of the sublimation systems disclosed with respect to **Figure 1** and **Figures 4-6** may be made. Thus, for instance, various of the alternative embodiments of the sublimation system of **Figure 1** that are described above may likewise be incorporated in the sublimation systems of **Figure 4**, **Figure 5** and/or **Figure 6**.

Additionally, while various embodiments of the present invention include mechanisms which facilitate maintaining a constant source-to-seed flow of Si, Si_2C and SiC_2, it will be appreciated that by such a constant flow is not necessary, and may not even be desired depending upon various other of the sublimation conditions, such as the temperature and/or pressure within the furnace.

In embodiments of the present invention, one or more silicon carbide electrodes are provided. It will be appreciated that these electrodes may be comprised solely of silicon carbide or, alternatively, may include other materials. For instance, in certain embodiments it may be preferred to coat a silicon carbide electrode with another material and/or provide a core of another material in the center of the electrode. Use of such another material might be employed to, for example, increase the conductivity of the electrode. The additional material provided in such silicon carbide electrodes may be of a material that sublimes at temperatures higher than the sublimation temperature for silicon carbide. In any event, it will be understood that the term "silicon carbide electrode" as used in the present application is intended to encompass silicon carbide electrodes which include materials other than silicon carbide.

In embodiments of the present invention, the silicon carbide electrodes are formed from a source silicon carbide powder. The source material may be grown, for example, by a chemical vapor deposition method of decomposing methyl tri-chlorosilane. Typically, both the mixture of polytypes in the source powder and the particle size distribution of the source powder will be selected to optimize the size and purity of the crystal that is to be grown. The source powder may be formed into an electrode by "sintering", which refers to a process whereby the source powder is placed into a mold and then subjected to a thermal treatment sufficient to partially, but not completely, melt the source powder particles. This

causes the source powder to congeal into a solid, and the particle sizes of the source powder and the thermal treatment conditions may be selected to achieve a desired density electrode (as the density of the electrode may impact the silicon carbide crystal grown during the sublimation process).

In additional embodiments of the present invention, the silicon carbide source powder may be n- and/or p-doped depending upon the type of semiconductors which are to be formed on the silicon carbide crystal grown during the sublimation process. Silicon carbide powder that is n-doped may be obtained, for example, by growing the powder in a nitrogen-rich environment, whereas p-doped silicon carbide source powder may be obtained by growing the powder in, for example, an aluminum-rich environment.

Figure 2 is a flow chart illustrating methods of growing crystals of silicon carbide according to embodiments of the present invention. Pursuant to these methods, a seed crystal of silicon carbide is introduced into the sublimation system (block **200**). As noted above, in applications where the silicon carbide is to be used for semiconductor fabrication, the seed crystal is typically monocrystalline. Either before or after introduction of this seed, first and second silicon carbide electrodes are also introduced into the sublimation system (blocks **202, 204**). These electrodes are positioned within the system such that they are separated by a gap. Once the electrodes are in place, an electric arc is established across the gap between the first and second silicon carbide electrodes (block **206**). This electric arc increases the temperature of at least a portion of each electrode to a temperature at which at least part of the electrode starts to sublime, thereby providing vaporized silicon carbide for crystal growth upon the seed crystal.

Figure 3 is another flow chart illustrating further methods of growing silicon carbide according to embodiments of the present invention. Pursuant to these methods, a seed crystal of silicon carbide is introduced into the sublimation system (block **220**). Either before or after introduction of this seed, first and second silicon carbide electrodes are also introduced into the sublimation system (blocks **222, 224**). These electrodes are positioned within the system such that they are separated by a gap. The interior of the sublimation system is then heated to a pre-selected temperature (block **226**). The seed is also heated to a high temperature, but this temperature is less than the temperature to which the walls of the furnace are heated (block **228**). At some point after the seed and electrodes are

introduced into the furnace, the pressure within the furnace is set to a pre-selected level (block **230**). Typically, both the furnace temperature, the seed temperature and the pressure within the furnace are set to levels that are selected to grow a selected polytype of silicon carbide having as few defects as possible and/or to optimize the rate of growth or the size of the crystal grown. Once the temperature and pressure are set, an electric arc is established across the gap between the first and second silicon carbide electrodes (block **232**). As discussed above, this may be accomplished by coupling an AC and/or a DC power supply to one or both of the electrodes. This electric arc increases the temperature of at least a portion of each electrode to a temperature at which the electrode starts to sublime, thereby providing material for crystal growth upon the seed crystal. As the portion of the first and second electrodes adjacent the arc start to erode away, the relative position of the electrodes is changed to maintain a gap of constant length (block **234**).

It will be appreciated by those of skill in the art that the acts depicted in **Figure 2** and **Figure 3** need not be carried out in the specific order indicated in the figure. For instance, the pre-selected pressure may be established (block **230**) prior to the heating described at blocks **226** and **228**. Likewise, the seed and first and second electrodes may be introduced in any order (blocks **220, 222, 224**), and the furnace could be heated before some or all of these elements are introduced. Accordingly, the order of the blocks in **Figure 2** and **Figure 3** are not intended to limit the scope of the present invention.

While the figures and descriptions herein disclose specific embodiments of the present invention, these embodiments are provided to ensure that the present disclosure is full and complete, and is not intended to limit the scope of the claims appended hereto. Thus, for example, the order in which steps of the sublimation processes disclosed herein are carried out may be modified without departing from the scope of the present invention, as those of skill in the art will realize that the timing of when specific materials are introduced into the sublimation system, or the order in which various portions of the furnace are heated or pressurized may be modified without significant impact on the disclosed processes.

In the drawings and specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms are employed,

they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following claims.